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Ceramics International 38 (2012) 3081–3088

CERAMICS INTERNATIONAL

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Oxidation behavior of carbon materials derived from a carborane- and silicon-incorporated polymer

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Received 13 October 2011; received in revised form 2 December 2011; accepted 2 December 2011
Available online 13 December 2011

Abstract

The oxidation behavior and oxidation mechanism of carbon materials containing silicon and boron elements (C–Si–B materials) were investigated at different high temperatures in air. The carbon materials were prepared by oxidative pyrolysis of the polymer precursor, carborane-incorporated poly(dimethylsilylene-ethynylenephenyleneethynylene) (CB-PSEPE), at 800, 1000, or 1200 °C for 1 h under static air. Homogeneous dispersion of silicon and boron components in the carbon matrix could be achieved in the carbon materials after the pyrolysis. The oxidation behavior of the C–Si–B materials during the oxidation process was studied. The evolution of elemental composition and morphology of the surface layers of carbon materials was monitored by X-ray photoelectron spectroscopy and scanning electron microscopy, respectively. The results imply that the formation of protective borosilicate layer in the surface is the main mechanism to provide remarkable oxidation resistance of the carbon materials. The obtained borosilicate layer with a self-healing property can withstand oxidation at 1000 °C in air.

Keywords: Polymer precursor; Carbon material; Borosilicate layer; Oxidation resistance

1. Introduction

Carbon materials such as graphite, carbon fiber and carbon–carbon composites possess excellent properties, including high strength at elevated temperatures, low density, high temperature tolerance, and low thermal expansion [1]. They have found wide applications in the high-temperature fields of aerospace and aviation. However, poor oxidation resistance restricts further usage of these materials. Oxidation reaction of conventional carbon materials occurs during their exposure to oxidizing environments above 450 °C, resulting in considerable deterioration of performance [2]. Thus, a number of oxidation protection methods have been proposed to solve the problem and extend the service life of carbon materials. Surface coating is a good choice to prevent carbon materials from oxidizing at high temperatures [3]. Silicides such as SiC, SiO_2, $MoSi_2$, $CrSi_2$ and borides such as B_4C, B_2O_3, BN, ZrB_2, W_2B_5 are promising candidates as oxidation resistant coatings [4–12]. They can be used separately or in combination. A problem in this method is that the surface coating could not provide further oxidation protection once it cracks due to thermal expansion mismatch between coating and carbon substrate [13]. In order to overcome this shortcoming, improvements have been made by mixing boride and silicide ceramic powders into carbon matrix, followed by pressureless sintering or hot-pressing of the mixture at high temperatures [14–18]. Combination of boron and silicon in matrix will form a borosilicate barrier during oxidation which is more effective for protection due to low viscosity and self-healing properties of borosilicate [19]. However, the difficulty in achieving a homogeneous distribution of silicide and boride ceramic powders in matrix and the poor sinterability between carbon and ceramic powders will influence the properties of the obtained materials. In addition, sintering and hot-pressing methods are not suitable for manufacturing products with complex shapes.

Polymer precursors have good shaping ability and processability. When the precursors containing inorganic elements such as silicon and boron are pyrolyzed, the inorganic elements will be homogeneously dispersed in the carbon matrix. Several kinds of polymers have been studied and evaluated as

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doi:10.1016/j.ceramint.2011.12.007

precursors for Si–B–C ceramic materials [20–22]. However, they are not carbon materials due to low carbon contents. Little attention has been devoted to the preparation of C–Si–B carbon materials through the pyrolysis of a single-source carbon-rich polymer precursor. Carborane-containing polymers possess excellent thermal and thermooxidative stabilities [23–28]. Recently, we have prepared a novel polymer precursor, *o*-carborane-incorporated poly(dimethylsilylene-ethynylenephenyleneethynylene) (CB-PSEPE), which contains silicon and boron elements in main chains [29]. CB-PSEPE can be crosslinked into a thermoset under heat (Fig. 1). In this paper, CB-PSEPE thermosets were pyrolyzed at the temperatures from 800 to 1200 °C in air to produce C–Si–B carbon materials. The oxidation behavior and mechanism of the C–Si–B materials during the oxidative pyrolysis were discussed based on the evolution of elemental compositions and morphology.

2. Experimental

2.1. Preparation of C–Si–B materials

Carborane-incorporated poly(dimethylsilylene-ethynylenephenyleneethynylene) (CB-PSEPE) and its thermoset were prepared by our previously published methods [29]. Typical crosslinked structures of CB-PSEPE thermoset are shown in Fig. 1.

The obtained CB-PSEPE thermosets with a size of about 5 mm × 5 mm × 2 mm were polished using emery paper, washed with acetone to remove contamination adhered to surface and dried in a desiccator overnight. The thermoset samples were heated to a set temperature (800, 1000, or 1200 °C) in static air at a heating rate of 2 °C/min, and then maintained at the temperature for 1 h. Then the samples were slowly cooled to room temperature (1 °C/min). The oxidative pyrolysis products for CB-PSEPE thermosets obtained at 800, 1000, and 1200 °C are designated as CB-PSEPE-800, CB-PSEPE-1000, and CB-PSEPE-1200, respectively.

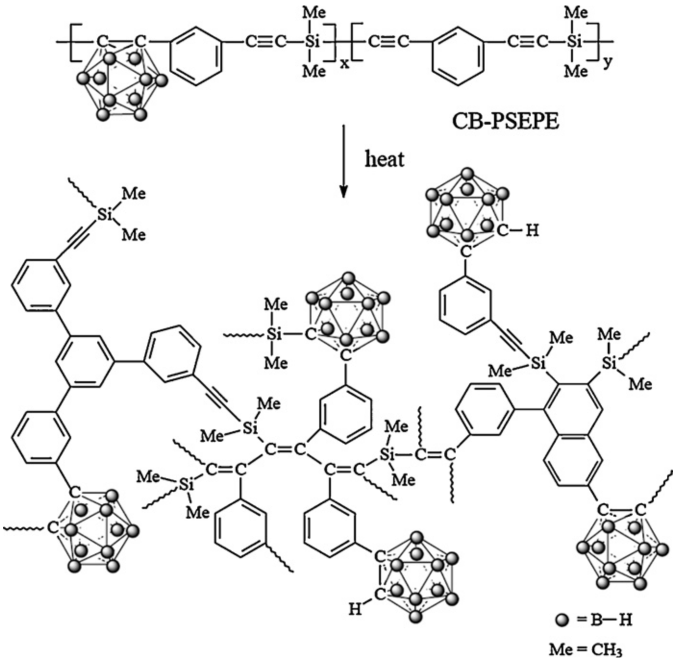

Fig. 1. Typical crosslinked structures of CB-PSEPE thermoset.

As a control, the non-oxidative pyrolysis experiments of CB-PSEPE thermoset samples with the size of 5 mm × 5 mm × 2 mm were also carried out at a set temperature (800, 1000, or 1200 °C) under an argon flow of 100 mL/min in a tube furnace with a heating rate of 2 °C/min. Then the samples were maintained at the temperature for 1 h and subsequently cooled with a rate of 1 °C/min to room temperature.

2.2. Characterization techniques

2.2.1. Weight loss

The weight changes before and after pyrolysis were recorded. Weights were measured using a Mettler digital analytical balance with ±0.1 mg accuracy. The weight change (ΔW %) of a sample was calculated by the equation: $\Delta W\,\% = (W_1 - W_0)/W_0 \times 100\%$, where W_0 and W_1 are the weights of the sample before and after pyrolysis, respectively.

2.2.2. Elemental analysis

Elemental analyses for C, O and H of CB-PSEPE thermosets and their oxidative pyrolysis products were conducted using LECO CS 600 Carbon/Sulfur Determinator, LECO TC 436 Nitrogen/Oxygen Determinator, and Elementar Vario EL III elemental analyzer, respectively. The thermosets and oxidative pyrolysis products were polished with emery paper to remove the surface layer and crushed into powders before analysis. Measurement of B and Si content was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Thermo Elemental IRIS 1000 spectrometer. The powder samples prepared mentioned above were decomposed by the alkaline fusion method with sodium hydroxide at 700 °C for 60–90 min in a nickel crucible. The amount of sodium hydroxide was 40–50 times the weight of sample to achieve complete digestion. Afterwards, the melt was dissolved with deionized water and then neutralized with hydrochloric acid. The obtained solution was diluted in a volumetric flask and analyzed by ICP-AES.

2.2.3. X-ray photoelectron spectroscopy (XPS)

XPS spectra were obtained on a Thermo Escalab 250 spectrometer with a monochromatic Al Kα radiation source ($h\nu = 1486.6$ eV, 150 W). The XPS data were collected from a spot dimension of 500 μm with a pass energy window of 20 eV. Each element composition was calculated from XPS spectra after correcting the relative peak areas by corresponding atomic sensitivity factors. The sum of the compositions of various elements present in the analyzed surfaces was equal to 100%. The atomic contents obtained from XPS data were converted into weight percentages.

2.2.4. Scanning electron microscopy (SEM)

SEM images were recorded on a JEOL JSM-6360LV microscope with an accelerating voltage of 15 kV. Prior to analysis, samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold using a JEOL JFC-1600 auto fine coater.

3. Results and discussion

3.1. Weight loss in pyrolysis process

The weight variations of the thermosets before and after pyrolysis were recorded as a function of temperature. Table 1 lists the residue yields of CB-PSEPE thermosets after pyrolysis at different temperatures in argon and air over a period of 1 h. After pyrolysis in argon, CB-PSEPE thermoset samples have residue yields above 82% in the temperature range from 800 to 1200 °C. When oxidized in air, CB-PSEPE thermoset exhibits excellent oxidation resistance, as shown in Table 1. Oxidation of CB-PSEPE thermoset at 800 °C for 1 h gives a residue yield of 86.2%, which is close to that of obtained after pyrolysis in argon (84.9%). Thus, the weight loss in the oxidative pyrolysis procedure is probably attributed to thermal degradation of organic components in the thermoset at high temperatures. Another experiments on oxidative pyrolysis of CB-PSEPE thermoset were conducted at 800 °C for 0–12 h in air to determine the long-term isothermal oxidative stability of the oxidation products. The related residue yields are tabulated in Table 2. After 12 h isothermal oxidation, the residue yield was 85.4%, which is only a minor decrease as compared with the value 86.2% (1 h oxidation). Therefore, the oxidation product obtained after pyrolyzing CB-PSEPE thermoset at 800 °C in air shows outstanding thermooxidative stability.

Small weight change is observed for CB-PSEPE thermosets in the temperature range from 800 to 1000 °C, as shown in Table 1. CB-PSEPE thermosets display similar residue yields of 83.4 and 82.0% at 1000 and 1200 °C in argon, respectively. However, the weight change between 1000 and 1200 °C in oxidative pyrolysis is noticeable, which reaches 24.6%. This implies that the oxidation product of CB-PSEPE thermoset can withstand oxidation at high temperatures of at least 1000 °C in air while it could not prevent further oxidation at 1200 °C.

3.2. Bulk compositions of oxidative pyrolysis products

When the CB-PSEPE thermosets were isothermally oxidized in air for 1 h at 800, 1000, and 1200 °C, the oxidations produced dense materials CB-PSEPE-800, CB-PSEPE-1000, and CB-PSEPE-1200, respectively. As compared with CB-PSEPE thermoset, the bulk composition of CB-PSEPE-800 changes slightly except for minor decreases in the contents of carbon, hydrogen and a small increase in oxygen content, as listed in Table 3. The decrement of carbon and hydrogen contents is probably due to the decomposition of organic groups in CB-PSEPE thermoset at high temperatures. The bulk composition of CB-PSEPE-1000 showed in Table 3 is almost the same as that of CB-PSEPE-800. CB-PSEPE-800 and CB-PSEPE-1000 samples have only a little lower carbon contents in comparison with the bulk compositions of the pyrolysis products of CB-PSEPE obtained at 800 and 1000 °C under argon in Table 4. These results indicate that the bulk materials of CB-PSEPE-800 and CB-PSEPE-1000 were well protected in the oxidation process.

When the oxidation temperature is elevated from 1000 to 1200 °C, the carbon content in the bulk material of CB-PSEPE-1200 is reduced obviously, along with the increase in oxygen content (Table 3). Moreover, the increase in the silicon content is also observed in the bulk of CB-PSEPE-1200. During the production of CB-PSEPE-1200, the oxidation-susceptible carbon element in the material would probably be severely oxidized due to limited protection against oxidation at 1200 °C in air. This would result in low residue yield, as evident in Table 1. Meanwhile, as compared with CB-PSEPE-800 and CB-PSEPE-1000, lower content of carbon but higher content of oxygen could also be expected in CB-PSEPE-1200, as shown in Table 3. The silicon element may be accumulated as a result of the higher thermal stabilities of silicon and its oxide. Thus, CB-PSEPE-1200 has the highest content of silicon among the three materials (Table 3). As a whole, the carbon contents of CB-PSEPE-800, CB-PSEPE-1000 and CB-PSEPE-1200 are all above 50%. Thereby, they are carbon materials. The changes in the contents of all elements are obvious when the temperature is elevated from 1000 to 1200 °C. Therefore, these carbon materials with silicon and boron elements prepared from CB-PSEPE polymer precursor could resist oxidation at temperatures up to 1000 °C, but they are only provided poor protection at 1200 °C.

Table 1
Residue yields of CB-PSEPE thermosets after pyrolysis at various temperatures for 1 h in argon or air atmosphere.

Temperature (°C)	Residue yield (%)	
	Air	Argon
800	86.2	84.9
1000	81.8	83.4
1200	57.2	82.0

Table 2
Weight changes of oxidation products obtained after pyrolyzing CB-PSEPE thermosets at 800 °C in air over different time periods.

	Time (h)			
	0	1	6	12
Residue yield (%)	87.4	86.2	86.0	85.4

Table 3
Bulk compositions of CB-PSEPE thermoset and its oxidative pyrolysis products determined by elemental analyses.

Sample	Bulk composition (wt%)				
	C	H	Si	B	O
CB-PSEPE thermoset	64.1	5.9	13.0	15.4	3.2
CB-PSEPE-800	56.4	2.8	13.4	16.9	9.0
CB-PSEPE-1000	55.2	2.3	14.1	17.5	9.9
CB-PSEPE-1200	50.3	2.2	21.3	14.7	13.4

Table 4
Bulk compositions of pyrolysis products of CB-PSEPE thermosets obtained at different temperatures under argon.

Temperature	Bulk composition (wt%)				
	C	H	Si	B	O
800 °C	62.5	1.9	15.3	17.8	3.9
1000 °C	63.2	1.0	14.4	18.5	2.1

3.3. *Surface compositions of oxidative pyrolysis products*

The surface elemental analyses of CB-PSEPE-800, CB-PSEPE-1000 and CB-PSEPE-1200 by XPS are tabulated in Table 5. As shown in Table 5, the element contents in the surface layer are totally different from the corresponding bulk composition (Table 3). The carbon content is much lower in the surface (below 7%) than in the bulk (over 50%). The main element accumulated in the surface layer is oxygen (around 60%). The surface composition of CB-PSEPE-1000 listed in Table 5 is similar as that of CB-PSEPE-800. As compared with CB-PSEPE-800 and CB-PSEPE-1000, the surface composition of CB-PSEPE-1200 shows a decrease in boron content but an increase in silicon content.

Besides the elemental contents, XPS can also provide chemical bonding information of the material surface. Fig. 2 shows the XPS survey spectra of the surfaces of the carbon-based materials CB-PSEPE-800, CB-PSEPE-1000 and CB-PSEPE-1200. As shown in Figs. 2(a) and 3, the peak for C 1s in the surface of CB-PSEPE-800 could be separated into three peaks and their binding energies are 284.7, 285.9 and 287.8 eV, which are attributed to C–C, C–O, and C=O bonds, respectively [27]. The O 1s spectrum shows a peak at 533.1 eV. The binding energy for the B 1s is 193.6 eV associated with B–O bond [30]. In addition, the peak located at 103.5 eV for Si 2p belongs to Si–O bond, which is similar to that present in silica [31]. The binding energies for the B 1s and Si 2p of the CB-PSEPE thermoset are 189.5 and 101.5 eV, which can be assigned to B–H and Si–C bonds, respectively. Thus, the structures of B–H in carborane and Si–CH_3 in silane units of CB-PSEPE thermoset are completely oxidized into boron oxide and silicon oxide in the surface of the material during the oxidation process, respectively. This result also illustrates the oxygen accumulation in the surface layer. The components of silicon oxide and boron oxide would form a borosilicate surface layer. The binding energies of B 1s and Si 2p found in CB-PSEPE-1000 and CB-PSEPE-1200 (Fig. 2(b) and (c)) are approximately 193.5 eV and 103.5 eV, which are also attributed to B–O and Si–O bonds, respectively. The XPS results indicate that borosilicate layers are presumably formed at the surfaces of CB-PSEPE-800, CB-PSEPE-1000 and CB-PSEPE-1200. However, boron oxide starts to evaporate at around 1000 °C at atmospheric pressure [32]. When the exposure temperature reaches 1200 °C, the evaporation of boron oxide increases considerably. Thus, the content of silicon oxide in the borosilicate surface layer of CB-PSEPE-1200 will be expected to increase due to the volatilization of boron oxide. This explains the increase of silicon content as well as decrease of boron content in the surface of CB-PSEPE-1200 in comparison with these of CB-PSEPE-800 and CB-PSEPE-1000.

Table 5
Surface compositions of carbon materials determined by XPS.

Sample	Surface composition (wt%)			
	C	Si	B	O
CB-PSEPE-800	6.3	25.1	6.1	62.5
CB-PSEPE-1000	5.9	25.8	6.6	61.7
CB-PSEPE-1200	3.1	33.0	4.2	59.7

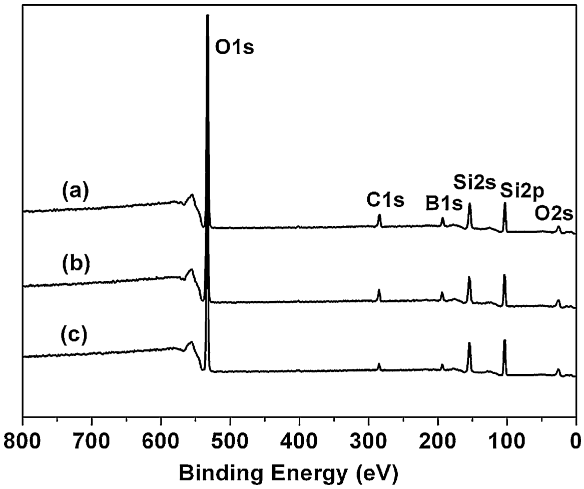

Fig. 2. XPS survey spectra of the surface of (a) CB-PSEPE-800, (b) CB-PSEPE-1000, and (c) CB-PSEPE-1200.

3.4. *Morphology of oxidative pyrolysis products*

Fig. 4 shows the fracture surfaces of pyrolysis products of CB-PSEPE thermosets obtained at 800 and 1000 °C under argon. After pyrolysis in an inert atmosphere, both of the obtained products demonstrate dense matrices and no protective layers are observed in the surfaces of the materials.

Fig. 5(a) shows the surface morphology of CB-PSEPE-800. After oxidation, many microscale pores can be observed on the surface, but the surface is still continuous. The oxidation proceeded by the inward diffusion of oxygen through the channels provided by the defects formed in the heating process [33]. The carbon in the matrix would escape in the form of CO or CO_2 [34], leaving a number of microscopic holes.

Fig. 5(b) demonstrates a dense and well-protected matrix. On the edge of the fracture surface of CB-PSEPE-800 product, a porous oxidized layer with a thickness of approximately 50 μm is apparently found. The layer formed entirely covers the whole surface of the material. When the carbon in the surface escapes in the form of CO or CO_2, the boron and silicon atoms are oxidized by the inwardly diffusing oxygen at high temperatures. The oxidation produces boron oxide and silicon oxide, as indicated by previously described XPS results. The oxides form continuous borosilicate layer in the oxidation process, until it is thick and dense enough to inhibit the penetration of oxygen. Once the oxygen penetration is reduced,

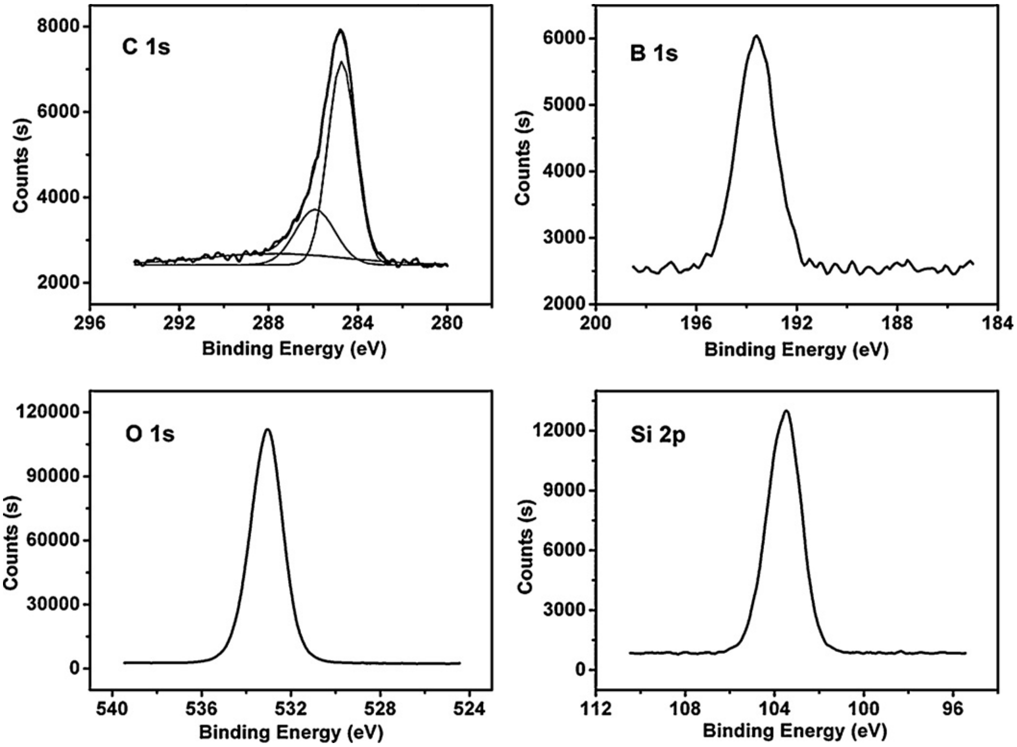

Fig. 3. XPS spectra for C 1s, B 1s, O 1s and Si 2p of the surface of CB-PSEPE-800.

the oxidation of matrix would be prevented. The formed layer is porous probably as a result of the high viscosity of borosilicate at low temperatures such as 800 °C. In any case, the formation of borosilicate protective layer in the surface is possibly the main mechanism to improve the oxidation resistance. This protective layer would possess a self-healing property during oxidation.

Fig. 6 displays SEM micrographs of the surface and fracture section of the CB-PSEPE-1000 material. The images reveal a different morphology from CB-PSEPE-800. As shown in Fig. 6(a), a smooth surface can be observed without obvious defects such as cracks and pores. Fig. 6(b) illustrates a dense and homogeneous borosilicate layer with a thickness of about 20–30 μm that covers the material surface. The bulk matrix is well protected and only a few voids are found. As compared with the porous layer of CB-PSEPE-800 in Fig. 5, the borosilicate layer in CB-PSEPE-1000 is much denser. The defects in the protective layer of CB-PSEPE-800 would be possibly eliminated at 1000 °C during oxidation. High temperature up to 1000 °C may be desirable to lower the viscosity of the borosilicate layer, which could provide enough flow through the layer to heal the defects. This is also important to facilitate self-healing for cracks of the material. These observations imply that the carbon material of CB-PSEPE can withstand high temperature of 1000 °C in oxidizing atmosphere.

The SEM image of the surface of CB-PSEPE-1200 demonstrates that the surface of the material is partially destroyed, as shown in Fig. 7(a). Some regions of the carbon material are evidently bare of any protective layer. The

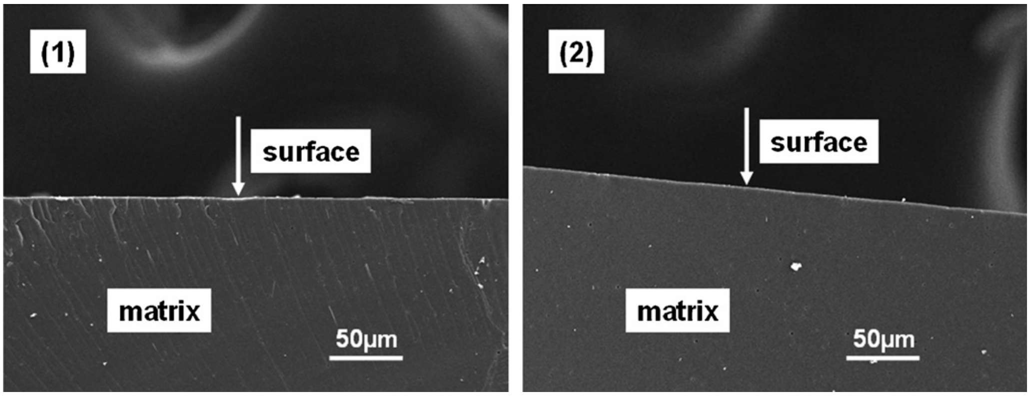

Fig. 4. SEM micrographs of fracture surfaces of pyrolysis products of CB-PSEPE thermoset obtained at different temperatures under argon: (1) 800 °C and (2) 1000 °C.

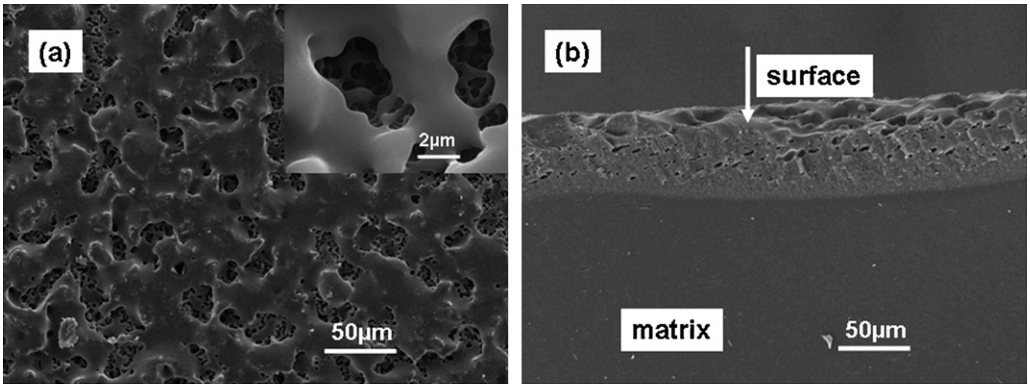

Fig. 5. SEM micrographs of CB-PSEPE-800: (a) surface and (b) fracture section.

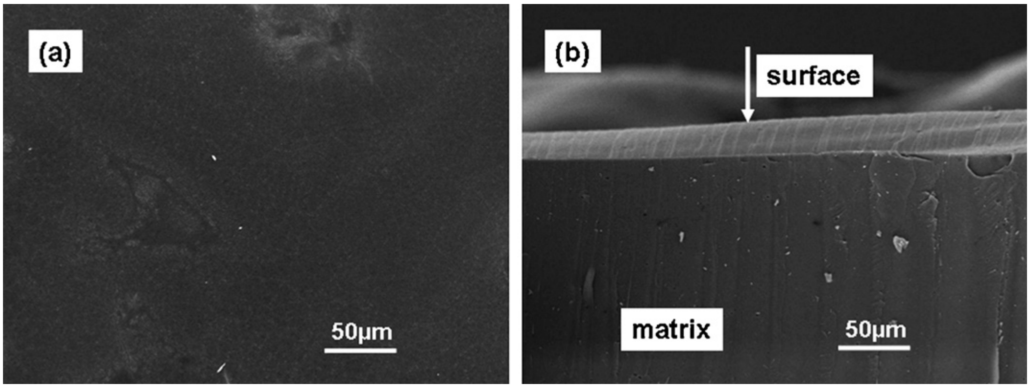

Fig. 6. SEM micrographs of CB-PSEPE-1000: (a) surface and (b) fracture section.

phenomenon is supported by the fracture surface near the edge of CB-PSEPE-1200 material in Fig. 7(b). The composition of B/Si ratio would affect the melting point and viscosity of the corresponding borosilicate [35]. The high amount of silicon oxide in the borosilicate layer of CB-PSEPE-1200 found in XPS results (Table 5) seems to increase the viscosity and restrict the free flow of the layer. Therefore, the protective layer possibly becomes ineffective at sealing the defects or even covering the whole surface of the material. The formation of an inhomogeneous protective film on the matrix results in the exposure of the unprotected matrix to air, as shown in Fig. 7(b). The naked matrix regions provide channels for rapid oxygen penetration, which causes extensive oxidative degradation. Thus, the matrix of the carbon material shows many voids after oxidation at 1200 °C.

3.5. Oxidation mechanism

According to the results mentioned above, we can postulate a model to describe the oxidation process of the carbon materials derived from CB-PSEPE thermosets at different high temperatures in air, as shown in Fig. 8. After oxidative pyrolysis at 800 °C for 1 h in air, a porous borosilicate layer with numerous of microscopic pores and channels is found in the surface of the carbon material (Fig. 8(a)). When the temperature is raised up to 1000 °C, the porous layer becomes

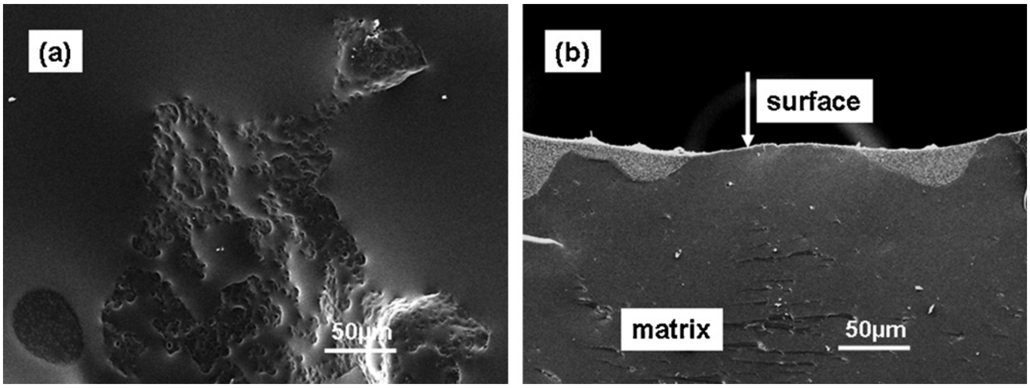

Fig. 7. SEM micrographs of CB-PSEPE-1200: (a) surface and (b) fracture section.

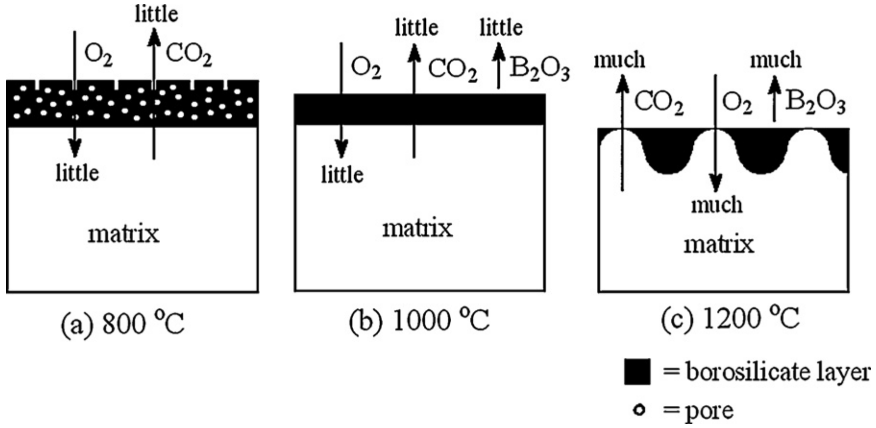

Fig. 8. Oxidation model of carbon materials obtained from CB-PSEPE thermoset at different temperatures in air.

dense and uniform due to lower viscosity of the borosilicate at the temperature (Fig. 8(b)). It offers good protection for the matrix. Oxidation at 1200 °C produces an uneven layer with naked matrix (Fig. 8(c)). Oxidation decomposition would further take place through the naked regions. The borosilicate with the high content of silicon oxide cannot protect the matrix against oxidation effectively.

4. Conclusion

The oxidation behavior of C–Si–B carbon materials derived from the polymer precursor, carborane-incorporated poly(-dimethylsilylene-ethynylenephenyleneethynylene) (CB-PSEPE), was investigated at different high temperatures in static air. CB-PSEPE thermosets produced carbon materials with residue yields of 86.2, 81.8, and 57.2% after oxidative pyrolysis at 800, 1000, and 1200 °C for 1 h, respectively. It is found that the formation of borosilicate protective layers is responsible for the excellent oxidation resistance of the C–Si–B materials. From 800 to 1000 °C, porous borosilicate layer will change into a dense film with self-healing ability. However, after isothermal oxidation at 1200 °C for 1 h, an inhomogeneous borosilicate layer with naked matrix would be obtained. The protective layer cannot cover the whole surface of the matrix to provide further protection. The polymer-derived C–Si–B carbon material is able to withstand oxidation up to 1000 °C in air. CB-PSEPE polymer is a promising precursor for oxidation resistant carbon materials.

Acknowledgements

We gratefully acknowledged the financial supports from the National Basic Research Program of China (Grant No. xx20303), the Shanghai Leading Academic Discipline Projects (B502) and Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application (Soochow University).

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